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The Effect of Contaminants
on the High Temperature Properties
of Carbide-Graphite Composites

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**The Effect of Contaminants
on the High Temperature Properties
of Carbide-Graphite Composites**

by

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ABSTRACT

The effect of the many process variables on the high temperature properties of hot pressed carbide-graphite composites has recently received wide attention. However, the effect of contaminants in the starting powders has not been mentioned. It was the intent of this program to investigate these variables holding the process variables constant. The results of the effect of contaminants are reported and show a correlation between Fe content and high temperature resistance to deformation.

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INTRODUCTION

Results from early development work at LASL¹ on NbC-C composites were obtained on specimens made primarily from a single lot of NbC powder. Data obtained on specimens made from several lots of powders from various vendors showed considerable spread in the test results. These specimens were all of the same composition and fabricated under identical conditions. Therefore, it was the intent of this program to determine the effect of contaminants in the as-received commercial powders on the high temperature properties of NbC-C composites.

RAW MATERIALS

The NbC powders used in this program represented seven lots obtained from four sources. The chemical analyses of these various lots of powder are presented in Table I. The graphite used was grade 1008 supplied by Great Lakes Carbon Company. This material was procured to a controlled particle size distribution specification as follows:

Mesh Size	Fraction %
+65	2.0
-65 +100	5.0
-100 +150	15.0
-150 +200	20.0
-200 +270	15.0
-270 +325	10.0
-325	33.0

TABLE I

CHEMICAL ANALYSES OF SELECTIVE NbC POWDER LOTS*

Elements	Lot 9	Lot 10E	Lot 13	Lot 13R**	Lot 14	Lot 15	Lot 17	Lot 17AR**	Lot 6
Nb	88.4%	88.5% ± 0.2%	88.5 ± .2%	88.9%	87.6%	87.3%	87.1%	88.5%	88.7%
Total C	11.08%	11.7%	10.77%	10.9%	11.4%	11.32%	11.5%	11.4%	11.2%
Free C	< 500	0.58%	770	< 500	900	0.14%	0.23%	0.2%	0.21%
C ₂	89 ppm to 0.21%	680 ppm to 0.11%	0.25%	0.25%	700	0.12%	0.14%	0.14%	.64%
Li	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Be	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
B	< 1	< 1	< 1	1	< 1	< 1	< 1	< 1	< 1
Na	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Mg	< 1	< 1	< 1	< 1	< 1	30	< 1	< 1	< 1
Al	< 10	30	< 10	< 10	< 10	< 10	200	< 10	< 10
Si	< 10	< 10	< 10	30	20	< 10	< 1	30	< 10
K	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Ca	20	< 5	< 5	< 5	< 5	300	10	< 5	< 5
Ti	300	< 10	< 10	< 10	500	< 10	< 10	< 10	< 10
V	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Cr	200	< 10	< 10	< 10	30	30	< 10	< 10	< 10
Mn	3	< 3	50	< 3	30	< 3	30	3	< 3
Fe	500	1000	3000	100	300	500	3000	500	50
Co	20	< 10	< 10	< 10	30	30	< 10	< 10	< 10
Ni	50	< 10	10	< 10	30	50	< 10	< 10	< 10
Cu	< 10	< 10	10	< 10	< 10	10	< 10	< 10	< 10
Zn	< 300	< 300	< 300	< 300	< 300	< 300	< 300	< 30	< 300
Sr	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Zr	< 100	< 300	< 100	100	< 100	< 100	500	< 100	< 300
Mo	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Ag	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Cd	< 3	-	-	-	-	-	-	-	-
Sn	< 50	< 50	< 50	< 50	50	< 50	< 50	< 50	< 50
Ba	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Ta	< 500	< 500	< 500	< 500	< 500	< 500	< 500	< 500	< 500
W	-	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
Pb	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
Bi	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

* All values ppm unless otherwise indicated

** Acid leached to remove Fe

A typical chemical analysis follows: 0.03% ash, 100 ppm Fe, 150 ppm Si, and the total of all others less than 200 ppm. Prior to usage the flour was screened to obtain the -150 +325 mesh fraction which was used in this work.

SPECIMEN PREPARATION

Hot Pressing

The charge formulation was based on weight percentages of the NbC and graphite used. The constituents were weighed to the nearest 0.1 g, placed into a glass jar with aluminum agitator wires, sealed and blended for 4 hr. The charge was then examined visually. If there was any evidence of segregation, the charge was blended for an additional 4 hr. The blend was removed from the jar and screened through a 50 mesh screen. At this point the blend was ready to load into a graphite die as a predetermined weighed charge. If for any reason the blend was allowed to sit around for longer than an hour or two before loading the dies, it was reblended for 20 min immediately prior to use.

Hot pressing was performed in a LASL designed induction heated hot press (Fig. 1). The pressings were 1.0 in. dia by approximately 1.3 in. long and were pressed in A-331 Stackpole graphite. Hot pressing was done at 3050°C and 3200 psi for 10 min at temperature. A typical pressure-temperature-time cycle is shown in Fig. 2.

The pressing assumed a very slight barrel shape as a result of the hot pressing and had to be cut from the die. The pressing was then machined to 1.0 in. dia by 1.0 in. long to remove any skin effect. Machining was accomplished by standard techniques using diamond tooling.

Fig. 1. LASL Designed Induction Hot Presses.

Fig. 2. Typical Pressure-Temperature-Time Cycle for Hot Pressing Dry Carbide-Graphite Composite Blends.

Testing

The machined specimens were weighed and measured, and then placed between the punches of an oversize die (as shown in Fig. 3) and tested. Two types of data were obtained. The single point test data were obtained by heating the specimens to 2700°C. At this point a load of 2000 psi was applied and held for 30 min after which the load was removed and the specimen cooled to room temperature. The specimens were removed from the die, measured and the amount (%) of deformation recorded.

Cumulative deformation data were obtained in a similar fashion; however, the specimens were first heated to 2000°C. At this point a load of 2000 psi was applied for 30 min after which the load was removed and the specimens cooled and measured. The specimens were then returned to the die and the procedure repeated increasing the temperature 200°C each time until 2600°C was reached. Above 2600°C the temperature was increased in 100°C increments until the cumulative deformation became excessive (arbitrarily set at 75%). The data were then plotted as a function of cumulative deformation versus test temperature.

DISCUSSION OF RESULTS

It was mentioned previously that considerable scatter in the data was obtained for specimens involving several powder lots. Figure 4 shows the scatter in the data for the seven powder lots involved. The earlier work mentioned previously involved specimens from powder lot NbC-9 which will be used as the basis for all comparisons in this report.

Since the fabrication procedures were essentially identical it was believed that this scatter was due to one

Fig. 3. Cross-Sectional View of the High Temperature Deformation Test Assembly.

Fig. 4. Vendor Qualification for 85 w/o NbC-15 w/o C M-2 Flour

or more contaminants in the as-received NbC powders. A quick look at the analytical results indicated that Lots NbC-13 and NbC-17, which showed the least resistance to deformation, were sub-stoichiometric, higher in oxygen and higher in Fe content than the other powder lots shown.

It was decided to plot single point test data for these various lots as a function of the various contaminants. The only trend as a function of increased contaminants was shown for Fe. Figure 5 is a plot of single point deformation for the various lots and shows an increase in deformation with increasing Fe content.

This effect of Fe, of course, was very undesirable and immediate concern was whether the Fe was combined in solution in the NbC or whether there was a film on the particles from the crushing and milling operation. A 500 g sample from each of the two lots highest in Fe was acid leached in hot $\text{HCl}:\text{H}_2\text{O}-1:1$, washed and dried. Specimens of the same composition were hot pressed and single point deformation tested. It is apparent from the test results, also shown in Fig. 5, that the Fe was a result of the crushing and milling operation. The chemical analyses of the leached powder (Table I) also confirm this observation since the Fe content is reduced from 3000 ppm to 100 ppm and 500 ppm for Lots NbC-13 and NbC-17, respectively.

To confirm these results further, additional specimens were tested. A cumulative deformation plot for these specimens is presented in Fig. 6. The data very dramatically show the effect of Fe on the high temperature deformation resistance. Metallographic examination of samples also reflects the effect of Fe content structure of the carbide matrix. The higher the Fe content the greater the network as is shown in Fig. 7. Metallography of the as-received powders showed no detectable second phases.

Fig. 5. Effect of Fe Content.

Fig. 6. Comparison of As-received and Leached Raw Materials.

300 ppm Fe

500 ppm Fe

1000 ppm Fe

Fig. 7. 85 w/o NbC-15 w/o C-No Binder.

SUMMARY

Deformation tests showed a profound increase in permanent deformation with increasing Fe content. This was the only trend observed for single point deformation tests versus the various contaminants in the as-received NbC powders.

It was apparent from the chemical analyses of the as-received and leached powders that the Fe was picked up during the crushing and milling stages of powder manufacture.

REFERENCE

1. Davidson, K. V., Riley, R. E., and Taub, J. M., Carbide-Graphite Composites, LA-3596-MS, July 14, 1966.